THE DETERMINATION OF THE TIME BETWEEN EXCITATION AND EMISSION FOR CERTAIN FLUORESCENT SOLIDS

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PHILIP FREDERICK GOTTLING

A DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

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THE DETERMINATION OF THE TIME BETWEEN EXCITATION AND EMISSION FOR CERTAIN FLUORESCENT SOLIDS

By Philip F. Gottling

Abstract

Time lag between excitation and emission of fluorescence by barium platino-cyanide and rhodamine.—The work begun in 1921 by R. W. Wood on the measurement of fluorescent intervals and phosphorescent times has been continued. The method of Abraham and Lemoine, somewhat modified, was used for determining the very short periods of time involved. The fluorescent light is polarized and then passed through a condenser, containing nitrobenzene as dielectric, which had begun to be discharged when the illuminating spark started. The later the light arrives the lower the average field of the condenser and the smaller the angular setting of the analyzing nicol to match the two images produced by a double image prism. The apparatus was calibrated by means of light reflected from a mirror at different distances from the spark. The interval of time between the occurrence of a spark and the emission of the fluorescent light excited by that spark, was found to be $(2.12 \pm .01) \times 10^{-7}$ sec. for barium platino-cyanide and $(2.11 \pm .14) \times 10^{-8}$ sec. for rhodamine.

Introduction

IT HAS been shown recently[1] that some fluorescent substances remain dark during a definite period of excitation, in other words, that the exciting energy was imprisoned for a short but definite and measurable interval of time within the fluorescent substance. In the case of mercury vapor, the period intervening between the beginning of the process and the emission of the light was found to be about 1/15000 sec. Similar observations made with barium-platino-cyanide indicated that not only was this interval of time less than 1/400,000 sec. but, furthermore, that the total duration of the phosphorescence, after the exciting incident energy ceased to fall upon the fluorescent substance, was also very short.

It was evident that the period of darkness for barium platino-cyanide was outside the range of the synchrono-phosphoroscope method employed. Some preliminary experiments were made employing the method of Abraham and Lemoine.

[1] R. W. Wood, Proc. Roy. Soc. A. 99, 362, 1921.

This method[2] makes use of the double refractive property of liquids when subjected to an electrostatic field. A condenser formed by immersing two metal plates in a liquid such as carbon bisulphide or nitrobenzene, is allowed to discharge through a spark gap. A Nicol prism is placed between the spark gap and the condenser, and, if the spark is viewed through the space between the condenser plates, it is impossible to extinguish the light by a second Nicol held close to the eye, unless the path over which the light must travel before reaching the condenser is increased the right amount, for example, by reflection in a mirror placed at the right distance.

It is evident from this that the double refraction of the liquid under these conditions varies with the time. This circumstance may be employed to measure the time which expires between the instant of occurrence of the spark and the beginning of the fluorescent light which its radiation excites, by adjusting the position of the mirror so that the fluorescent light just does not pass through the second or analyzing Nicol. The distance between this position and the corresponding position when the light from the spark is at the point of extinction, when divided by the velocity of light, would give the time the fluorescent substance remains dark.

Description of Apparatus

For the particular problem at hand, however, it was found advantageous to elaborate on the simple arrangement and method just described by introducing a double image prism into the optical path of the light between the condenser and analysing Nicol. The final electrical circuit and optical arrangement employed is indicated by Fig. 1, an arrangement very similar to that proposed by Lord Rayleigh for the measurement of very short times.[3]

The spark gap P was connected through a resistance R to the condenser K containing nitrobenzene, which will be referred to as the Kerr cell. The latter alone gave a poor spark, but by connecting a Leyden jar A in parallel with the first circuit, as shown in the figure, a brilliant spark was obtained. The condensers A and K, charged intermittently by an ordinary spark coil C operated by a twelve volt storage battery, were discharged at the spark gap P. The capacity of the Kerr condenser was 49.7×10^{-11} farad. The inductance L of the K-R-P circuit was approximately 1100 cm, and the value of the resistance R was usually greater than 100 ohms. With 300 ohms as the resistance R, the time constant

[2] Abraham and Lemoine, Compt. Rend., p. 206, 1899

[3] Rayleigh, Scientific Papers, Vol. V, p. 190

of the K-R-P circuit was 1.49×10^{-7} sec. The period of the spark and Leyden jar, i.e. the A-P circuit was 1.19×10^{-7} sec.

Light from the spark gap P was polarized by the Nicol N_1. The double image prism D was placed between the Kerr cell K and the analyzing Nicol N_2, and so orientated as to give only one image of the narrow slit S when K was disconnected from the electrical circuit. The Nicol N_2 was then turned to the position of extinction of this image. Call this the zero position of N_2. Introduction of the Kerr cell into the electrical circuit caused the restoration of one of the images, namely that one whose plane of vibration was parallel to the short diagonal of the analyzing Nicol. Turning N_2 through a small angle restored the other image, and two positions of N_2, obtained by turning it clockwise in

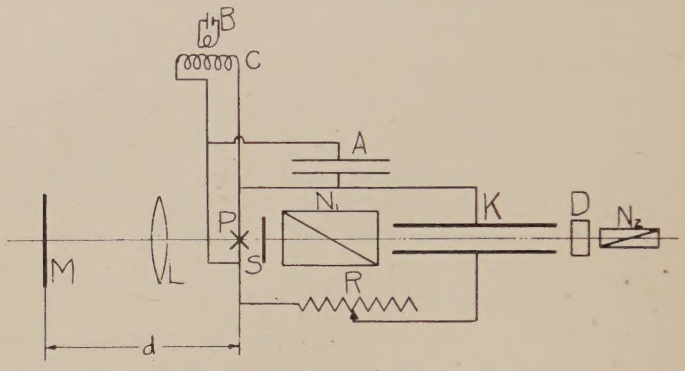

Fig. 1. Diagram of apparatus.

one case and counter clockwise in the other case, could be found at which the intensities of the two images appeared the same. The angles α through which N_2 must be turned to arrive at these positions, are opposite in direction and equal in value. If instead of illuminating the slit S by the spark directly, the light is first made parallel by a lens L, is reflected in a mirror M, and is then focused on the slit S, it is found that the angle α is different for different positions of the mirror M.

Theory

We will consider the electrical sequence of events of the circuits in Fig. 1 and the resulting optical effects. The interrupter of the primary circuit of the induction coil C induces a high potential in the secondary which in turn charges the condensers A and K. This charging process continues until the breakdown potential of the spark gap P is reached. At the occurrence of the spark, an oscillatory discharge of A through P begins, while the discharge of K through the resistance R and P is non-

oscillatory if, for the circuit K-R-P, $R^2/4L^2 > 1/LK$, where L is the inductance of the circuit and K the capacity of the Kerr condenser. This condition was maintained during the experiment. The electric field acting upon the nitrobenzene under these conditions will, therefore, vary with the time t in some such manner as shown in Fig. 2.

Now it may readily be shown that the setting α of the analyzing Nicol necessary for balance, depends upon the field strength alone and not upon the intensity of the light. This was also verified experimentally. Hence if the light train begins to pass through the condenser K at the instant t_1 (Fig. 2) when the field strength is E_1, the corresponding setting of the Nicol will be a function of the average value of the field which obtains from t_1 to the end of the light train. If the light begins to pass at some later instant t_2, the average field strength will be less and the setting of the Nicol will be correspondingly less. In order to determine the relation between α and t, the instant when the light begins to arrive was

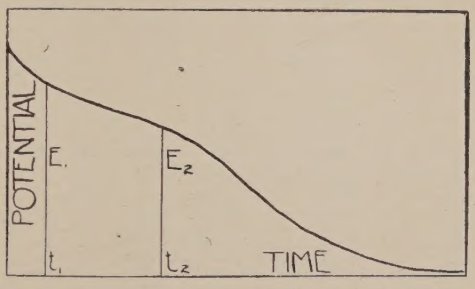

Fig. 2. Time variation of the potential across the Kerr condenser.

varied by varying the position of the mirror M from which the light has been reflected. If, then, light from some fluorescent solid placed close to the spark P is observed, a setting of the Nicol will be obtained which, when compared with the relation between α and t previously determined, will give the time lag between the excitation and emission of light for that substance.

Experimental Procedure

The method of measuring the dark time of any fluorescent substance is to determine the variation of 2α with the distance of the mirror M when some high resistance, as 1000 or 1500 ohms, is used as the damping resistance R, and to determine the difference between the angle 2α for the fluorescent substance in question and that obtained by viewing the spark directly under the same conditions. If this difference is large, say 5° to 10°, evidently the period of darkness for this substance is long, for with such a high resistance in the circuit described above, the angle 2α

varies by about five degrees as the mirror M is moved from the spark to a position 45 meters from the spark. For a case of this kind results obtained when R is two hundred ohms or less are not reliable since for such a low resistance the plates of the K-condenser discharge almost completely in the time required for light to travel ninety meters (see Curve E, Fig. 3), and the cell would consequently only slightly restore the fluorescent light, thus making it difficult if not impossible to balance

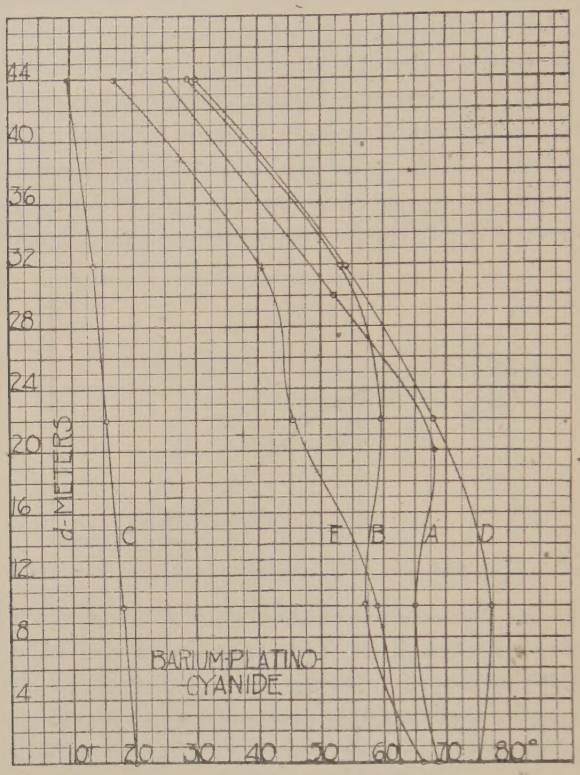

Fig. 3. Results with barium-platino-cyanide.

the intensities of the two images. In such a case the resistance should be kept as large as 400 ohms or more and the fluorescent light would be restored accordingly (see Curve C, Fig. 3).

If, however, with 1000 ohms in the circuit the angle 2α for the fluorescent substance examined differs by only a degree or two from the angle obtained from observations made directly on the spark, the time interval in question is of the order of magnitude of that required for light to pass twice the distance from the spark to a mirror about twenty meters away. In such a case lower resistance must be employed so as to increase

the rate of decay of charge on the plates of the Kerr cell and thus increase the rate of change of restoration of the cell.

The shape of the curves obtained showing 2α as a function of the distance between the spark and mirror, depends, in the electrical arrangement shown in Fig. 1, not alone upon the resistance R, but also upon the width of the spark gap. Curves A, B, D, E, Fig. 3, which were taken with a spark gap of approximately 1 cm, show oscillations. When the spark gap was reduced to 2 or 3 mm curves such as D, Fig. 4, were

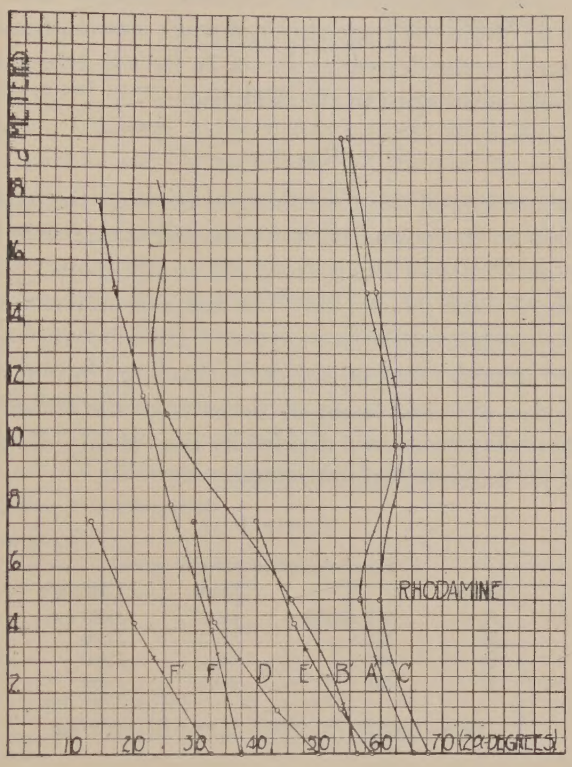

Fig. 4. Results with rhodamine.

obtained. In instances where the dark time is very short these oscillations are highly undesirable, for there are two and sometimes three points on the curve whose abscissas are the same angle 2α as obtained for the fluorescent substance. If, however, the resistance is changed, and another curve and angle 2α for the fluorescent substance is determined, there will again be two or three points on this new curve whose abscissas equal the new angle 2α for the fluorescent substance. One of these points only, however, will have the same ordinate as one of the three points of

the preceding curve, so that, even if the oscillations exist, it is still possible to determine a short time interval.

The method, therefore, is to determine approximately the interval with a high resistance R in the electrical circuit, and then more accurately with a lower resistance if necessary. The best conditions are obtained when the nature of the resulting curve is such as to have a rapid change in 2α in the region of the angle of the fluorescent substance. At the same time the latter angle should be not only fairly large, a circumstance which is consistent with brightness of the restored images, but should also differ by 10 or 15° from the angle obtained when viewing the spark directly; then the error in the determination of 2α for the fluorescent material gives a relatively small error in the dark time.

Results

Five determinations of the time interval between the absorption and emission of light in the case of barium-platino-cyanide were made, using four different resistances varying from 200 to 400 ohms. Curves A, B, C, D, E in Fig. 3 show the results. The abscissas of curve C are diminished by 40° to avoid crowding the curves. The following table gives the angle obtained in each case and the corresponding position of the mirror which would give the same angle as taken from the curve. Twice the average of these distances when divided by the velocity of light gives the dark interval for barium-platino-cyanide.

Table 1

Barium-platino-cyanide

Curve	R	Angle	Distance
A	300 ohms	48.7°	3180 cm
B	250	53.2	3196
D	300	54.1	3180
E	200	40.6	3169
			Mean 3181 cm

$$T = 2d/v = 2\times 3181/3\times 10^{10} = (2.12 \pm .01)\times 10^{-7}\text{sec.}$$

The value of d obtained from curve C, although agreeing as well as could have been expected with the other values, was not used in calculating the mean, for in this case the resistance was 400 ohms and the curve so steep that a variation of $\frac{1}{2}$° in the angle results in a variation of 75 cm in the distance d. The maximum deviation from the mean value is about $\frac{1}{2}$ per cent. The time interval is $(2.12 \pm .01)\times 10^{-7}$ sec.

The next substance examined was rhodamine in a solution of acetone, acetic acid and glycerine. The fluorescence of rhodamine was bright red and no difficulty was experienced in matching intensities of the two images. The percentage accuracy in this case was, however, not as good

as in the case of barium-platino-cyanide. The mean value 316 cm for d yields $(2.11 \pm .14) \times 10^{-8}$ sec. as the period of dark time for rhodamine.

TABLE 2

Rhodamine

Curve	R	Angle	Distance
F	200 ohms	53.5°	325 cm
A′	150	59.0	313
B′	200	54.0	320
C′	100	62.0	303
D′	80	37.3	302
E′	80	47.9	338
F′	80	43.3	312

Mean = 316 cm

$T = (2.11 \pm .14) \times 10^{-8}$ sec.

The curves obtained in determining the time interval for rhodamine are shown in Fig. 4. Curve B' is there drawn to the same scale of abscissas as the other curves in the Figure but to half scale in the ordinates. The abscissas of F and F' are diminished by 20° to avoid crowding the curves. Particular attention is called to A' and C' which show the oscillations referred to above. In each of these cases there are three points whose abscissas are the angle 2α obtained from the observations made on rhodamine, the ordinate of only one of A' is the same as the ordinate of one of the three points of C′. This ordinate, moreover, agrees very well with those obtained from the curve showing no oscillations.

The author wishes to acknowledge his appreciation to Professor R. W. Wood for his valuable suggestions, and to Dr. Frank V. Grimm who prepared the nitrobenzene.

PHYSICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
May 16, 1923.

BIOGRAPHICAL NOTE

PHILIP FREDERICK GOTTLING, son of Bernhard F. and Hattie Gottling, was born in Baltimore, Maryland, on the 7th of December, 1897. He received his preparatory education at the Baltimore City College, graduating in 1915. In the same year he entered the School of Engineering of the Johns Hopkins University and received the degree of Bachelor of Engineering in 1919. He then entered the Physical Department of the graduate school, holding a Scholarship in that department for the years 1919-1920, and taking courses under Professor Ames and Associate Professor Pfund in Physics, and Professors Cohen and Murnaghan in Mathematics. The following year he held a position as student engineer at the General Electric Company, Schenectady, New York. He again held a scholarship in the Physics Department of the Johns Hopkins University during the years 1921-22 and 1922-23, attending lectures by Professors Ames and Wood in Physics and Professor Murnaghan in Mathematics. He received the degree of Master of Arts in June 1922.